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As-Deposited Superconducting Thin Films by Electron Cyclotron Resonance-Assisted Laser Ablation for Application in Micro-Electronics

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A method for the growth of as-deposited superconducting thin films which combines YAG-laser ablation and oxidation by an electron cyclotron resonance (ECR)-excited oxygen plasma is described. It is demonstrated by depositions on YSZ and $SrTiO_3$ substrates that this one-step method is compatible with the requirements of large surface homogeneity, low substrate temperature and low oxygen partial pressure. The method is therefore well suited for applications in micro-electronics.

KEYWORDS: High-T_c superconducting films, YBCO thin film preparation, laser ablation, ECR-oxidation

§1. Introduction

The deposition of high T_c superconducting YBaCuO thin films has now advanced to the stage where several techniques (sputtering, ablation, evaporation, molecular beam epitaxy (MBE), chemical vapor deposition (CVD), etc.) produce high quality layers. Geerk *et al.*[1] classify those deposition processes in their review article into two categories:

—the first is a three-step procedure depositing the film in the amorphous phase, bringing it to the tetragonal form $Y_1Ba_2Cu_3O_6$ at high temperature (>900°C) and intercalating the oxygen ($Y_1Ba_2Cu_3O_7$) at lower temperature (~400°C) and elevated oxygen pressure;

—the second is a two-step procedure (often called "*in-situ* preparation"), realizing a deposition in the tetragonal phase at temperatures in the region of 650°C–750°C and therefore only requiring an oxygen intercalation step at lower temperatures in an oxygen atmosphere. An equivalent of this last step is the slow cooling down in oxygen ambient after deposition by allowing oxygen to fill the deposition chamber.

To our knowledge, up to now no one-step process in which the YBCO layer is deposited in its superconducting phase has been realized. It is clear that such a deposition method would offer new possibilities for applications. Indeed, if cooling down of the YBCO layer in oxygen pressure is not needed to make it superconducting, deposition of other layers can be continued at the same substrate temperature and in the same vacuum conditions.

More in general can be stated that if the superconducting films aim at micro-electronic applications, their production process must satisfy some severe requirements depending on the application:

—large surface homogeneity is needed for use in off-chip interconnections;

—the deposition temperature must be reduced to 550°C–600°C to broaden the range of substrates on which good high-T_c material can be grown (*e.g.* low loss, low ε_r dielectrics for microwave applications or semiconductor substrates for integration with existing GaAs and Si technology);

—the film must preferentially be superconducting in the as-deposited state without exposure to a high oxygen pressure post-deposition step (one-step procedure), so that multilayer structures can be formed in-situ.

The deposition technique which will be described here is a combination of an ECR (Electron Cyclotron Resonance)-plasma oxidation and a Nd-YAG laser ablation leading to the first production method of superconducting films fulfilling the above requirements of deposition at low substrate temperature on large surfaces in a one-step procedure.

§2. Experimental Set-Up

The deposition chamber made of stainless steel is cylindrical in shape (diameter of 50 cm, height of 70 cm). It has several flanges attached to it: one at the top for the heated substrate holder and pressure gauge, one at the bottom for vacuum pumping and some in a horizontal plane. One of these flanges holds the rotating superconducting YBCO pellet which is 5 mm thick and has a diameter of 20 mm. On the opposite flange the introduction chamber and transfer system for the substrate are mounted. Four other flanges have transparent windows, one for the incoming laser, one for Rheed diagnostics in front of the electron gun, and two others to enable side viewing of the plume and of the mounting of the substrate.

The rotating target pellet is located at a distance of 7 cm facing the substrates. The substrates are clamped onto a metal block and are heated by direct radiation. The frequency tripled Nd: YAG laser (Quanta Ray GCR-3) at 355 nm has a pulse energy of 0.2 J and a pulse duration of 6 ns. The laser beam is not focused, has a diameter of 7 mm and thus produces a fluence of 0.5 J/cm^2. Irradiation is carried out at 10 Hz and is incident near 15° to the target surface normal.

Two large flanges (200 mm in diameter) in front of

each other and normal to the target-substrate axis contain coils generating a magnetic field distribution inside the chamber. In the center of one of these a coaxial antenna emits microwaves of 2.45 GHz delivered by a continously variable output generator (up to 300 W) via a waveguide structure fitted with 5 mobile circuit terminations for impedance matching. The oxygen gas is introduced to the vessel through the coaxial conductor of the antenna and regulated by means of a microleak. The partial oxygen pressure used in these experiments is measured by turning a Bayert-Alpert gauge to the place where the substrate is located during deposition and is maximally 5×10^{-4} Torr. At this pressure plasma ignition is possible. Electron resonance conditions are achieved at 10 cm from both sides of the substrate where the magnetic field value is 875 G. The plasma is transported along the magnetic fieldlines and the substrate. The 875 G regions act as magnetic mirrors and the plasma is confined to a cylindrical region of 50 cm long and 6 cm in diameter which is visible due to its yellow light.

§3. Preparation of Films

Films were deposited on polycrystalline rough Yttrium stabilized ZrO_2 (YSZ) and on polished (100) $SrTiO_3$ substrates. The deposition temperature was measured by a thermocouple mounted at the backside of the substrate in the environment of the heating filament. As was verified by observing the melt of a dot of Aluminum placed onto the substrate surface, these temperatures must at least be reduced by 50°C to estimate the substrate temperature. Due to the transparency of the substrates it is impossible to determine the temperature at their surface by the pyrometer. At the beginning of each deposition the substrate was heated. The background pressure was 2×10^{-6} Torr. Plasma was then started with an oxygen partial pressure of 5×10^{-4} Torr and an injected microwave power of 60 W. Immediately the laser ablation of a superconducting YBaCuO pellet started. Deposition lasted four hours. In proving that we developed a one-step method it is thus essential that we do not increase the oxygen pressure after deposition and during slow cooling. Therefore, the laser was stopped and simultaneously the substrate temperature was quenched by reducing the heater current to zero. The cooling rate (Fig. 1) was so fast that extra uptake of oxygen was impossible. Moreover, the plasma pressure of 5×10^{-4} Torr was not increased during the cooling period. After maximum 15 minutes, as the substrate temperature was lower than 200°C the vessel was vented by air and the film was immediately taken out. Without any post treatment films were mounted in a closed cycle refrigerator for 4 probe resistance measurements. Four copper pins at 5 mm distance in a standard square configuration were pressed onto the YBaCuO film without any intermediate contact layer.

Two Japanese groups have also used an ECR-plasma for oxidation of YBCO films during growth, one in combination with evaporation out of Knudsen cells[2] and one in combination with electron beam evaporation.[3] However the construction of the ECR-system is different: in our set-up no discharge tube nor extraction potential

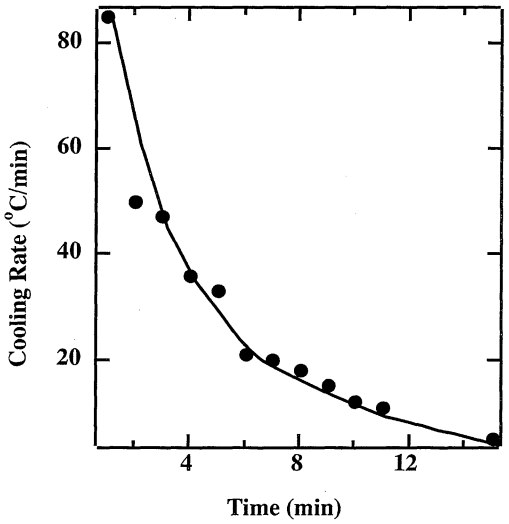

Fig. 1. Cooling rate of the substrate temperature after deposition of the YBaCuO layer.

to accelerate the ions is used. Moreover, both groups report that a supplementary oxygen intercalation step after deposition is necessary to make the films superconducting again leading to a two-step process.

§4. Results

4.1 *Surface homogeneity*

The center of the ablated plume was directed to the bottom left of a 2 inch polycrystalline YSZ substrate. The deposition was carried out as described in the previous section at a substrate temperature of 620°C. In Fig. 2(a) is indicated on which spots of the film Rutherford Backscattering Spectrometry (RBS) was performed to analyse its thickness and composition. A He^{2+} ion beam of 2.270 MeV was used to bombard the film and backscattered particles were detected at an angle of 165°. Spectra were fitted using the SCATT (Charles Evans and Associates, U.S.A.) simulation program. Most representative examples of the resistance curves measured on the same spots are shown in Fig. 2(b).

The thickness of the film is 1000 nm and varies less than 10% in a circle with radius of 2 cm. At a radial distance of 3 cm, resp. 4 cm the thickness has decreased with 30%, resp. 60%.

The composition of the top layer inside the circle with a radius of 4 cm (*e.g.* A, B, C in Fig. 2(a)) is $Y_1Ba_2Cu_3O_{7-y}$, but is Cu deficient outside this circle (*e.g.* D) corresponding with a collection angle larger than 30°. It is in agreement with the angular distribution measurements of laser-ablated particles of Lynds[4] that the Cu concentration at such detection angles is too low.

Fitting of the RBS spectrum of point B (Fig. 3(a)) reveals an interface layer of about 250 nm where the YBaCuO film and the YSZ substrate have reacted. The depth resolution is somewhat degraded by the film roughness, but there is an apparent change in stoichiometry in the interface region (Fig. 3(b)). Barium seems the most mobile metal atom in this film, followed by copper. The presence of the Ba-rich layer at the film-YSZ interface can be explained by the migration of Ba to this region which is enhanced to relieve interfacial stress

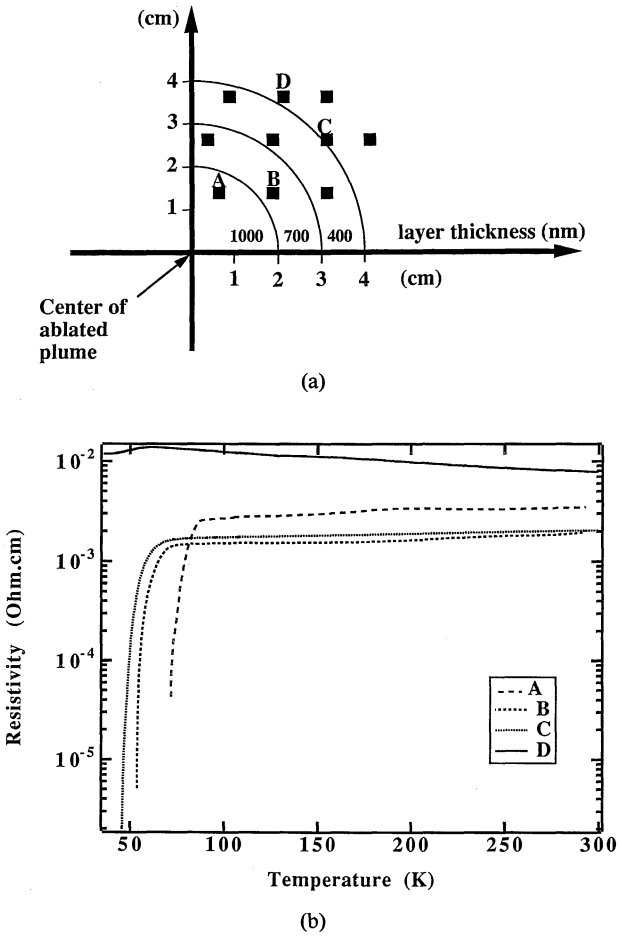

Fig. 2. (a) A quarter of the ablated superconducting material plume is deposited on an YSZ substrate and analysed by RBS on the indicated spots. (b) Resistivity curves as a function of temperature, measured in spots A, B, C and D.

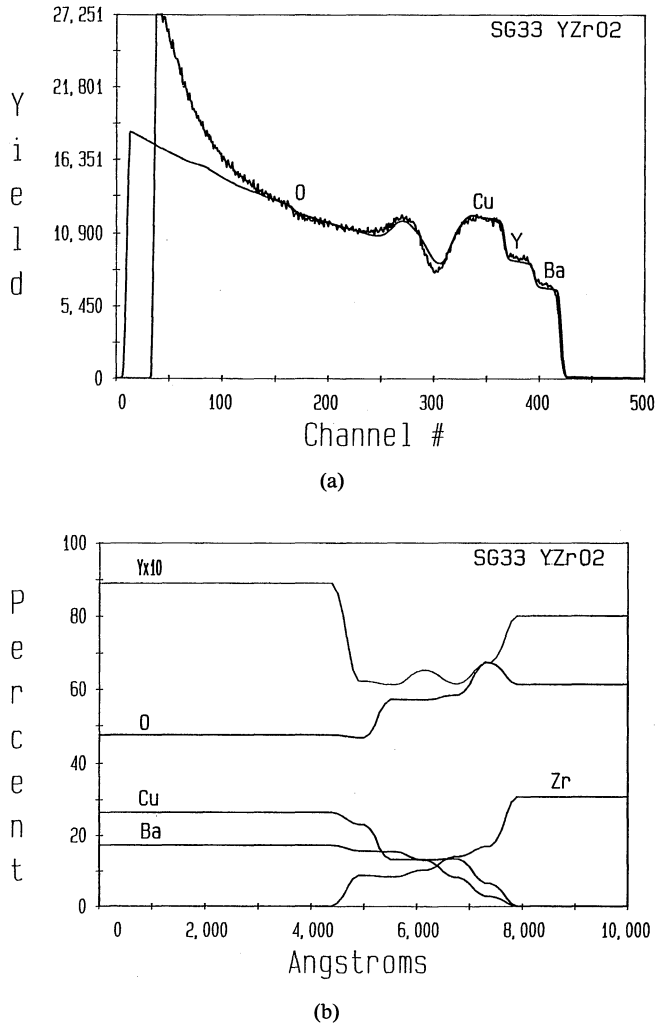

Fig. 3. (a) Measured and fitted RBS spectrum on spot B. (b) A composition diagram as a function of depth deduced from the RBS fit.

during the cooling process. The data of Fig. 3(b) indicate that after the migration of barium to the interface Cu begins to migrate into the region between the film and the Ba-rich layer.

For the spots A, B and C, T_c increases with thickness due to the relative thickness increase of the 1-2-3 layer compared to the interface layer. Indeed, as the critical current in these granular films is very low, the current density decreases with increasing layer thickness, leading to higher T_c values.

4.2 *One-step deposition at reduced substrate temperature and oxygen pressure*

The film produced on YSZ for the surface homogeneity study in previous section had very good superconducting properties, taken into account that the underlying substrate has a rough and polycrystalline surface. The resistance curve of the film is drawn in Fig. 2(b) and shows an onset temperature of 90 K and an offset temperature of 75 K. As this film deposition was performed as described in §3 by quenching the substrate temperature and without oxygen pressure increase, it is proven that the simultaneous use of ECR-plasma and laser ablation lead to as-deposited superconducting films. Regarding this result on polycrystalline YSZ, it was hoped that deposition on polished monocrystalline $SrTiO_3$ could lead to even better characteristics.

The center of the ablated plume was directed to a 7.5 mm × 7.5 mm (100) $SrTiO_3$ substrate which was heated by direct radiation. The resistance versus temperature behaviour of the ablated film was studied as a function of the substrate temperature T_s (Fig. 4(a)) during deposition with a fixed oxygen partial pressure (5×10^{-4} Torr) and injected power (60 W) in the plasma. The low T_c values at the lowest deposition temperatures below 560°C indicate that not enough oxygen was included. On the other hand, the low T_c values at deposition temperatures above 600°C show that the oxygen pressure of 5×10^{-4} Torr is too low to prevent oxygen outdiffusion at these temperatures. The resistance curve of these films shows an onset at 90 K, but a long tail is caused by an oxygen deficient phase in the film. This became clear as the film with the same growth parameters but with a supplementary step consisting of a post-treatment in oxygen atmosphere at 450°C during 30 minutes before cooling down to room temperature, exhibited a higher T_c around 90 K. In the intermediate deposition temperature region (between 560°C and 600°C) it is possible to produce an as-deposited superconducting film. To be sure that the use

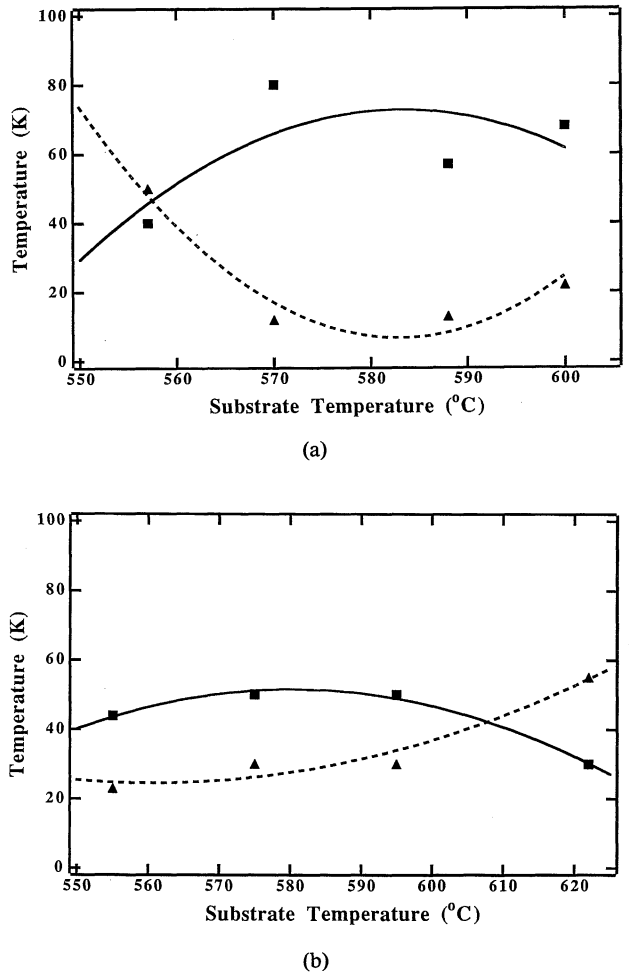

Fig. 4. Offset temperatures (squares) and transition width (onset-offset temperature) (triangles) of superconducting films deposited at different deposition temperatures and with an injected microwave power in the oxygen plasma of 60 W (a) or 300 W (b).

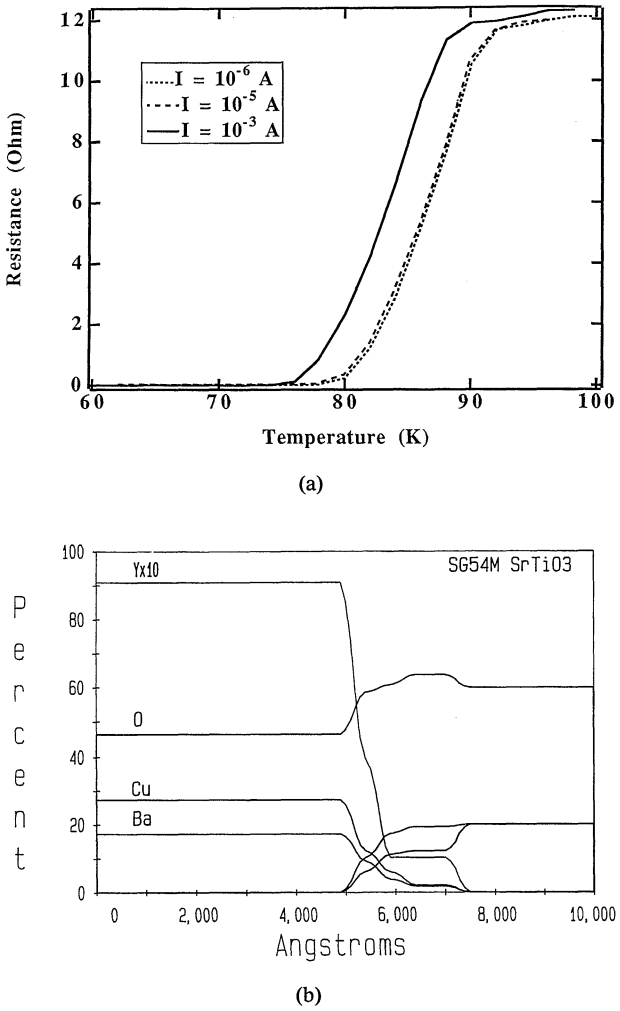

Fig. 5. (a) Resistance curves as a function of temperature and injected current in the film. (b) Composition diagram as a function of depth deduced by the RBS fit of experimental data.

of the ECR-oxygen plasma in which the substrate is immersed is the key of the succesful one-step growth, a film was prepared under exactly the same conditions but using neutral oxygen at nominally the same flowrate. This film had a semiconductor behaviour from 300 K to 5 K. As is well known, the ECR microwave plasma ignition occurs at low pressures (10^{-4}–10^{-5} T) compared to RF or DC plasma and has much higher efficiency in producing very reactive ions and atoms. The abundance in the ECR-plasma of activated oxygen species with a higher chemical reactivity than molecular oxygen explains why complete oxidation of the film occurs at lower substrate temperature and at lower oxygen pressure compared to the use of neutral oxygen. Such a plasma enhances chemical reactions making it possible to synthesize films at lower temperature, although it is not clear yet whether the activated oxygen species are excited molecular, atomic or ionic oxygen. Up to now the best characteristic of an YBaCuO film deposited on $SrTiO_3$ by this one-step process is an onset temperature of 90 K and an offset temperature of 80 K.

The same study was performed at a higher injected microwave power of 300 W, leading to films with lower T_c values as displayed in Fig. 4(b). It seems that the parameters of the oxygen plasma, —although not fully understood at the moment—, play an important role in determining the quality of the deposited layer. Therefore, future study will concentrate on plasma diagnostics to try to understand its influence. Different polarisation effects of the substrates are a possible explanation for the fact that lower microwave power during the growth of YBCO films on $SrTiO_3$ lead to better superconducting films.

In Fig. 5(a) the resistance curve of the film grown at a deposition temperature of 570°C and in an oxygen plasma of 5×10^{-4} Torr is shown as a function of the current. Although critical current densities were not measured yet, it is clear that the values are still very low. It was not possible to channel through this layer and the fit of the random RBS spectrum revealed an important interface layer of 180 nm as is clear in the composition diagram of Fig. 5(b). The formation of the cracks in these films proves the existence of strong tensile stress at the interface during the cooling process. The same mechanism can lead to the Ba migration. A correlation between interfacial layer thickness and degree of crack

formation is evident. These findings are in agreement with the publication of Venkatesan *et al.*[5] in which the interface is studied by Auger profiling.

§5. Conclusion

It has been demonstrated that superconducting YBaCuO films can be deposited in one step at low substrate temperature (570°C) in an oxygen ECR-plasma at low partial pressure (5×10^{-4} T). This opens new possibilities towards the in-situ production of multilayers as well as towards the integration of superconducting films with classical micro-electronics (GaAs, Si). As the YAG-laser ablation and plasma oxidation provide large superconducting areas, off-chip interconnections become a possible application.

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Note added in proof—In the paper of K. Yamamoto et al. (APL57(199O) 1936) published after submission of our paper, it is proposed that in the presence of an ECR plasma which contains a certain amount of atomic oxygen the phase diagram of oxygen content versus temperature of YBCO is changed. As a result they suggest: "It may be possible to perform in situ orthorhombic growth under some experimental conditions (low-temperature deposition, very high atomic flux)." This last remark is confirmed by our experiments.